Subunit Interactions in Neutral, Mono-, and Dicationic Forms of Pyridine-Fused Bis(10-oxacorrole)

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Porphyrinoids encompass a wide range of structures, including porphyrins, corroles, and expanded porphyrins, with tunable aromatic, non-aromatic, or antiaromatic properties dictated by their structure and electron delocalization. Linking porphyrinoid units to form dimers offers a strategy for modulating their properties.[1, 2] Fused systems exhibit strong electronic interactions between subunits, altering spectroscopic and redox behaviors, as seen in the cases of pyridine-fused bis(norcorrole)s[3] or heterodimer consisting of aromatic porphyrin and antiaromatic norcorrole.[4] The versatility of norcorrole in many modification reactions allows it to be also used in oxidative ring expansion. Here, this led to oxacorrole, which we further extended. In this work, we present the synthesis and characterization of novel pyridine-fused bis(oxacorrole) dimers, with emphasis on their redox behavior. We reveal an interplay between the aromaticity and antiaromaticity of these dimers during redox processes by providing a detailed exploration of the electronic state of the reduction and oxidation products based on ESR, UV-Vis-NIR, and NMR data, supported by theoretical calculations.

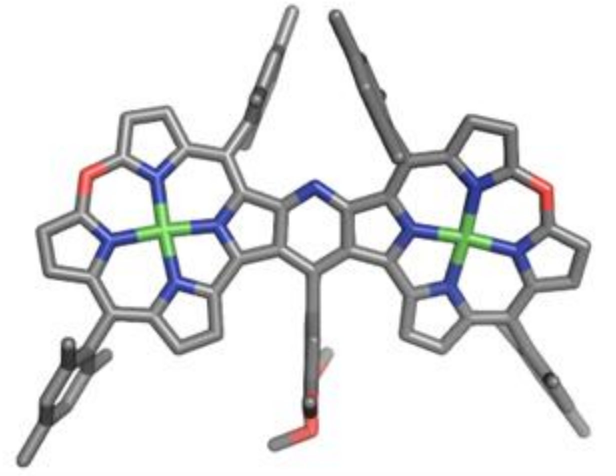

Figure 1. Exemplary structure of one of the bis(oxacorrole) dimers obtained.

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